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# Wastewater disinfection by neutral pH photo-Fenton: The role of solar radiation intensity

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ABSTRACT

Advanced oxidation technologies for wastewater treatment have been recognized as promising solutions for disinfection. Among them, solar photo-Fenton at near neutral pH is being proposed as alternative disinfecting technology. This study analyses the role of two solar energy parameters, solar UVA irradiance (intensity in terms of $W\,m^{-2}$) and accumulated solar UVA energy dose per unit of volume of treated water ($Q_{UVA}$, in terms of $kJ\,L^{-1}$), on wastewater disinfection by solar photo-Fenton at neutral pH. For this purpose, a systematic study of the influence of three UVA irradiance levels (10, 20 and $30\,W\,m^{-2}$) and different accumulated energy doses (0.6, 1.4, 1.8, 2.5, 3.2 and $3.7\,kJ\,L^{-1}$), achieved at the irradiances assayed, was performed under real sun conditions. These parameters were evaluated during the inactivation of *E. faecalis* by solar photo-Fenton operating at neutral pH with 20 mg $Fe^{2+}\,L^{-1}$ and 50 mg $H_2O_2\,L^{-1}$ in simulated secondary effluent from a municipal wastewater treatment plant, keeping the temperature at $25.0 \pm 0.2\,^{\circ}C$. Results clearly shown that an increase in irradiance improved the bacterial inactivation rate giving rise to the following first order rate constants: $0.025 \pm 0.002$, $0.057 \pm 0.001$ and $0.089 \pm 0.004\,min^{-1}$ at 10, 20 and $30\,W\,m^{-2}$ respectively. Furthermore, the hydrogen peroxide consumption rate increased with irradiance: $(2.3 \pm 0.4)\cdot10^{-3}$, $(4.6 \pm 0.8)\cdot10^{-3}$ and $(6.0 \pm 0.8)\cdot10^{-3}\,mM\,min^{-1}$ at 10, 20 and $30\,W\,m^{-2}$, respectively. These results showed that, under the tested conditions, *E. faecalis* inactivation rate by solar photo-Fenton at neutral pH was limited by solar UVA irradiance. Consequently, first order kinetics for *E. faecalis* inactivation *versus* the accumulated energy dose was observed, regardless of the UVA irradiance value used. These results show that it was possible to monitor a solar photo-Fenton plant for wastewater disinfection on a $Q_{UVA}$ dose basis instead of treatment time, when microorganism inactivation is photo-limited.



## 1. Introduction

Current issues on water scarcity and pollution of fresh water resources have awoken the scientific community's interest in exploring efficient and sustainable wastewater treatments. Recently, advanced oxidation processes (AOPs) have been studied as alternative for the inactivation of highly resistant pathogens in real wastewaters [1–5]. The promising results found for removal of bacteria, fungi and viruses by the photo-Fenton process have paved the way for a new water disinfection method. The efficiency of this process is based on the production of non-selective and highly oxidizing hydroxyl radicals ($HO^{\bullet}$). They are generated when hydrogen peroxide reacts with iron during the photo-Fenton reactions (Eqs. (1)–(8)). Under UV–vis radiation, the ferric ions ($Fe^{3+}$) produced in the presence of hydrogen peroxide (Eq. (1)) are photo-converted to ferrous ions ($Fe^{2+}$), increasing the hydroxyl radical generation rate (Eq. (2)).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + HO^{\bullet} \quad (2)$$

$$R^{\bullet} + O_2 \rightarrow R - O_2^{\bullet} \quad (3)$$

$$R - O_2^{\bullet} + H_2O \rightarrow ROH + HO_2^{\bullet} \quad (4)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (5)$$

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$$HO_2^{\bullet} \rightarrow O_2^{\bullet-} + H^+ \quad (6)$$

$$O_2^{\bullet-} + H_2O_2 \rightarrow O_2 + HO^{\bullet} + HO^- \quad (7)$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (8)$$

Although the radical production is favored at acidic pH, previous studies have also shown high bacterial inactivation efficiency using photo-Fenton at neutral pH with a consequent reduction in the cost of reagents [5]. In a recent study, Ruales-Lonfat et al. [6] discussed the role of different iron oxides on the solar water disinfection. They reported that iron hydroxides act as catalysts of the heterogeneous photo-Fenton process at neutral pH (Eqs. (9) and (10)):

$$> Fe^{3+}OH + h\nu \rightarrow > Fe^{2+} + HO^{\bullet} \quad (9)$$

$$> Fe^{2+} + H_2O_2 \rightarrow > Fe^{3+} + HO^- + HO^{\bullet} \quad (10)$$

where $>Fe^{2+}$ and $>Fe^{3+}$ denote the iron species in solid phase [6].

Reactive oxygen species (ROS) generated during the photo-Fenton reactions (Eqs. (1)–(10)) cause detrimental effects to microorganisms. ROS, mainly hydroxyl radicals, inflict damage on bacteria cells through direct external membrane structure; oxidize proteins; harm the integrity of DNA molecules and disrupt several metabolic activities compromising microorganism viability, leading to bacterial inactivation [1].

Most of the studies on solar photo-Fenton for organic contaminant removal, deal with mineralization rate or pollutant conversion rate as a function of two equivalent parameters: the total amount of solar UVA energy received per unit volume of treated water, $Q_{UVA}$, kJ $L^{-1}$; or the normalized exposure time calculated for standard conditions of solar UVA irradiance of 30 W $m^{-2}$, $t_{30W}$, min [1]. These parameters are reliable for the evaluation of organic matter degradation in water for different solar reactors (regardless of the concept design used *e.g.* for stirred tanks or tubular reactors) because pollutant removal rate is proportional to the amount of photons entering the system needed to photo-activate the photo-Fenton process [1].

This idea cannot be assumed to be completely valid for microorganism inactivation. Although solar photo-inactivation processes for water disinfection have proven to be more efficient when a higher solar energy dose is received in the system [7], there is not a simple relationship between microorganism photo-inactivation rate and solar exposure time, energy received, or dose applied. Previous contributions on heterogeneous photo-catalytic disinfection with titanium dioxide [8], demonstrated that $Q_{UVA}$ plays an important role in the disinfection process. Usually, assessment of microorganism inactivation by solar advanced oxidation processes is carried out using the parameter $Q_{UVA}$. Experimental time is not often used for this purpose, when irradiation is provided by natural sunlight, as solar irradiance values vary constantly. In the case of solar photo-inactivation processes, particularly photo-Fenton, there are very few contributions investigating aspects of radiation [9]. All the cited studies show different ways to consider the influence of solar radiation. Moreover, these processes involve distinct intrinsic mechanisms; as while some of them are mainly driven by hydroxyl radicals (AOPs), others are dominated by UVA absorption followed by ROS generation (solar photo-inactivation). However, until now, there has been a lack of research to elucidate which parameter is more adequate for the kinetic characterization required to make predictive models for reactor design and up-scaling for large wastewater disinfection systems.

With this aim in mind, this paper is focused on clarifying the roles of both solar energy parameters: accumulated energy dose (in terms of total energy received in the system per unit of volume, kJ $L^{-1}$) and irradiance (solar intensity, in terms of W $m^{-2}$) in the disinfection of wastewater during the solar photo-Fenton process at neutral pH. To this end, a systematic study on the influence of different natural solar irradiances (10, 20 and 30 W $m^{-2}$) and UV doses (0.6, 1.4, 1.8, 2.5, 3.2 and 3.7 kJ $L^{-1}$) was performed. Temperature was maintained at a constant of 25.0 ± 0.2 °C. $Fe^{2+}$ and $H_2O_2$ concentrations were 20 and 50 mg $L^{-1}$ respectively. These were reported as being the most favorable conditions to disinfect real wastewater by photo-Fenton at pilot plant scale [5]. *Enterococcus faecalis* was used as model microorganism since it showed higher resistance to the treatment than other typical microbial pollution indicators like *E. coli* [10]. Simulated wastewater treatment plant effluent (SWWTPE) was used as the water matrix at pH 8 in all experiments. Additionally, in order to follow the photo-Fenton reaction, hydrogen peroxide consumption was monitored throughout all the experiments.

## 2. Experimental methods

### 2.1. Bacterial strain, inoculum preparation and quantification of samples

*E. faecalis* CECT 5143 was acquired from the Spanish Culture Type Collection (Colección Española de Cultivos Tipo, Valencia, Spain). Cultures of *E. faecalis* were grown in *Streptococcus* selective Broth and Agar media (Biolife) and incubated at 37 °C with constant agitation in an orbital shaker at 150 r.p.m. for 24 h. *E. faecalis* suspensions were harvested in stationary phase by centrifugation at 3000 r.p.m. for 10 min and washed three times with saline solution (0.9% NaCl) obtaining a final bacterial concentration of $10^6$ CFU $mL^{-1}$ (determined by optical density at 600 nm). The required stock volume was added to the saline solution (prepared with sterile Milli-Q water) in order to avoid osmotic stress and a detrimental effect on cell viability during the experiments. In order to ensure that the initial concentration of bacteria was $10^6$ CFU $mL^{-1}$, a sample of the initial suspension was taken before the reactor was exposed to sunlight. This control sample was kept at room temperature for the duration of the experiment and it was then plated. The samples taken during the experiment were enumerated using the standard plate count method through 10-fold serial dilutions. Volumes of 1 mL of the diluted samples were spread onto 140 mm-diameter plates with *Streptococcus* selective Broth (30.6 g $L^{-1}$) and agar (15 g $L^{-1}$) in triplicate, before being incubated at 37 °C overnight. The detection limit was found to be 1 CFU $mL^{-1}$. Catalase (Sigma–Aldrich, USA) was added to the samples in order to eliminate residual hydrogen peroxide.

### 2.2. Water matrix

The effects of temperature and water matrix composition on the bacterial inactivation by photo-Fenton process have been studied previously [11,12] All experiments in this study were carried out at constant temperature (25.0 ± 0.2 °C) to rule out any thermal effects on the inactivation results. A simulated secondary effluent of a municipal wastewater treatment plant (SEWWTP, [12]) was used in order to avoid daily variability of the real wastewater effluent. The composition of SEWWTP was as follows: $NaHCO_3$ (96 mg $L^{-1}$), NaCl (7 mg $L^{-1}$), $CaSO_4{\cdot}2H_2O$ (60 mg $L^{-1}$), urea (6 mg $L^{-1}$), $MgSO_4$ (60 mg $L^{-1}$), KCl (4 mg $L^{-1}$), $CaCl_2{\cdot}H_2O$ (4 mg $L^{-1}$), peptone (32 mg $L^{-1}$), $MgSO_4{\cdot}7H_2O$ (2 mg $L^{-1}$) and meat extract (22 mg $L^{-1}$), which yielded 20 mg $L^{-1}$ of DOC. The pH of this water was always around 8 at the start of the experiments and varied very lightly to pH 7.

### 2.3. Experimental setup

Jacketed stirred tank reactors which allowed water temperature to be controlled (Schott-Duran, Germany) were used under natural solar light (Fig. 1). The temperature was kept constant at

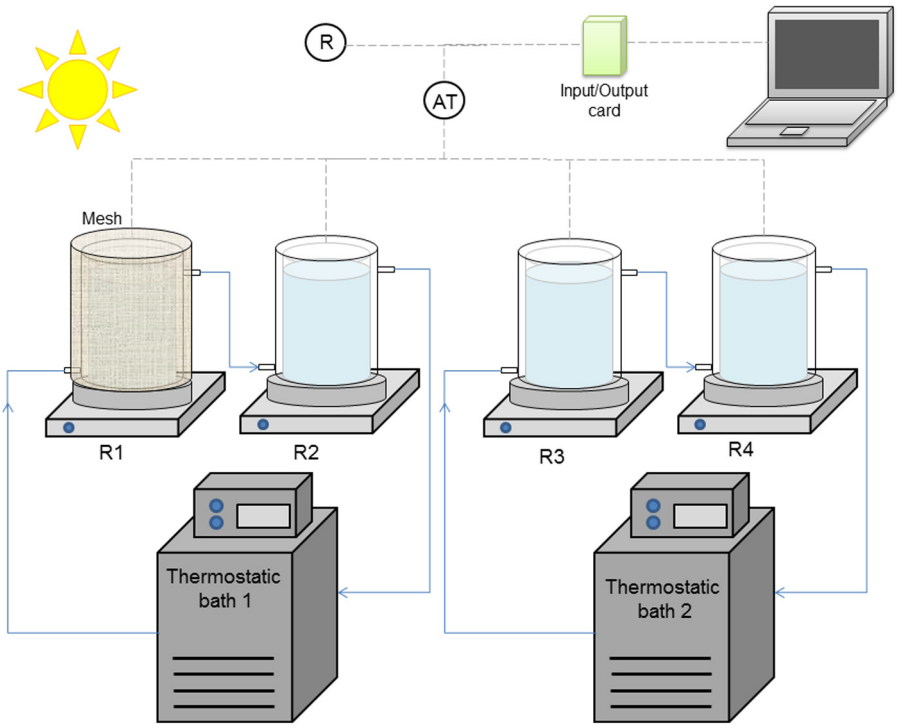


**Fig. 1.** Experimental setup for *E. faecalis* inactivation by solar photo-Fenton.

25.0 ± 0.2 °C using a thermostatic bath (thermo Scientific NESLAB RTE7). The dimensions of the reactors were: 20 cm height, 10 cm internal diameter and 1.25 L volume.

Different solar UVA incident radiation values were applied under real sun conditions on clear sunny days. Two meshes of 1.0 and 1.5 mm pore size were used which partially filtered solar irradiance as and when necessary. These meshes were placed around and on the top of the reactors. UV radiation was measured using a global UV radiometer (Delta Ohm, LP UVA 02 AV) with a spectral response range from 327 to 384 nm, mounted on a horizontal platform, providing data in terms of incident UV radiation ($W\,m^{-2}$). The UVA irradiance and temperature data were acquired throughout the entire experiment by a data acquisition card (LabJack U12) connected to a computer. The UVA irradiance data were used to calculate the accumulated solar energy incident on the photo-reactor for each sample during the experiment per unit volume ($Q_{UVA}$, $kJ\,L^{-1}$) according to Eq. (11):

$$Q_{UVA} = \sum_n U\bar{V}A_{n-1} \cdot \frac{A_r}{V_t} \cdot (t_n - t_{n-1}) \quad (11)$$

where $t_n$ is the experimental time for sample $n$, $U\bar{V}A_{n-1}$ is the average of solar $U\bar{V}A$ ($Wm^{-2}$) at exposure time $t_n - t_{n-1}$, $A_r$ is the illuminated area of the reactor ($m^2$) and $V_t$ is the total volume of treated water (L). The efficiency of a solar reactor depends in particular on the solar radiant power absorbed by the reaction system and therefore on the incident solar radiant power. The ferrioxalate actinometry [11] was chosen to estimate these values for solar these reactors. In order to apply Eq. (11), the illuminated area of the reactor vessel exposed to solar irradiation was determined after ferrioxalate actinometry finding this value was equal to 0.025 $m^2$, which was lower than the total external area of the reactor.

### 2.4. Wastewater disinfection by photo-Fenton under natural solar radiation

Experiments were carried out around noon in order to avoid sharp irradiation variations and keep incident radiation almost constant at 10, 20 and 30 $W\,m^{-2}$ of UVA (Fig. 2). Different solar exposure times (Table 1) were needed to obtain the required values of accumulated energy dose (0.6, 1.4, 1.8, 2.5, 3.2 and 3.7 $kJ\,L^{-1}$). Four reactors (Fig. 1) containing 1 L of SEWWTP were spiked with an initial bacterial concentration of $10^6$ CFU $mL^{-1}$. After homogenization, oxidizing reagent and catalyst were added (50 and 20 $mg\,L^{-1}$ of $H_2O_2$ and $Fe^{2+}$, respectively) to the reactors at the same time. These photo-Fenton reagent concentrations led to rapid bacterial inactivation without reagent limitation, as observed before [5,12,13]. After that the reactors were uncovered and exposed to natural sunlight. Every combination of irradiation and exposure time was carried out three times to guarantee high statistical significance of the obtained results. When the desired UVA dose was achieved and water samples were taken and evaluated, the reactor

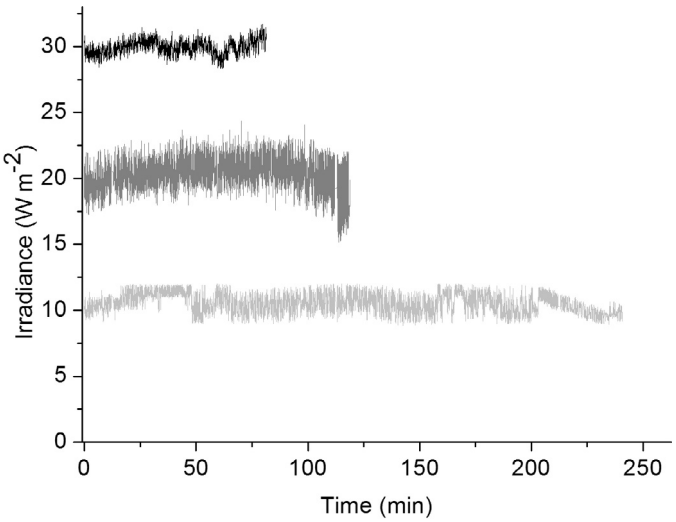


**Fig. 2.** Solar irradiance profiles during experimental runs performed at average UV irradiance values of 10.5 ± 0.7, 19.9 ± 1.3 and 29.9 ± 0.6 $W\,m^{-2}$.

**Table 1**
Exposure time (min) necessary to obtain the different values of accumulated energy dose ($Q_{UVA}$) from 0.6 to 3.7 kJ L$^{-1}$ reached at the three fixed values of solar irradiation (10, 20 and 30 W m$^{-2}$) for each experiment.

| | $Q_{UVA}$ (kJ L$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | 0.4 | 1.4 | 1.8 | 2.5 | 3.2 | 3.7 |
| $I_{UVA}$ (W m$^{-2}$) | | | | | | |
| 10 | 40 | 80 | 120 | 160 | 200 | 240 |
| 20 | 20 | 40 | 60 | 80 | 100 | 120 |
| 30 | 15 | 30 | 40 | 60 | 70 | 80 |

was covered and the experiment was continued in the dark for a period of 60 min. During the dark period no decrease in *E. faecalis* concentration was observed.

### 2.5. Analytical determinations

Ferrous sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$, Panreac, Spain) was used to obtain $Fe^{2+}$ concentrations of 20 mg L$^{-1}$. Iron concentration was analyzed by the o-phenantroline standardized method according to ISO 6332. Hydrogen peroxide (33%, w/v aqueous solution, Panreac, Spain) concentration was measured with titanium (IV) oxysulphate solution (Riedel-de Häen, Germany) spectrophotometric method at 410 nm (method DIN 38 402 H15). All water samples were filtered with 0.2 μm syringe-driven filters (Millex®, MILLIPORE) prior to iron analysis to measure only the dissolved iron in the samples.

## 3. Results and discussion

The role of UVA irradiance, $I_{UVA}$ (W m$^{-2}$), *versus* the accumulated solar energy, $Q_{UVA}$ (kJ L$^{-1}$), on bacterial inactivation by solar photo-Fenton at neutral pH was investigated. Previous research showed that the simple use of sun light under the same experimental conditions only induced a 1-log decrease in 180 min while photo-Fenton accounted for complete water disinfection for the same dose [5]. Fig. 3 shows *E. faecalis* inactivation with treatment time for the three irradiances used in this study, pooling all the data obtained in 18 experimental runs. The decrease in *E. faecalis* CFU count followed first order kinetics compatible with the Chick-Watson disinfection model (Eq. (12)):

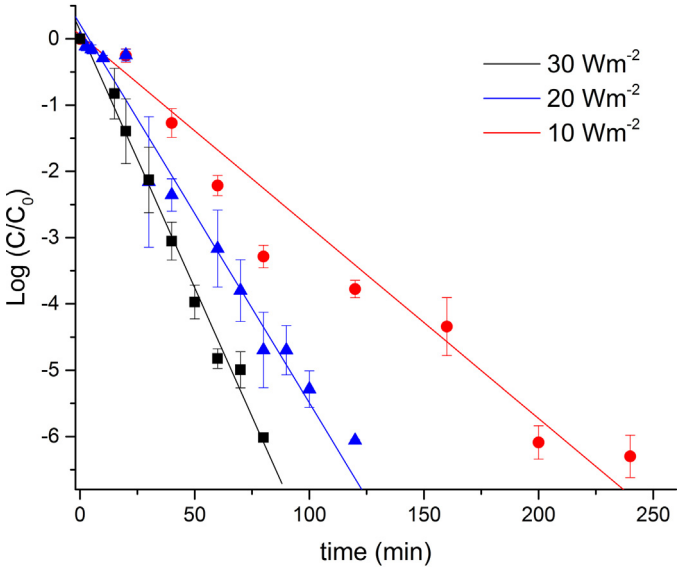


**Fig. 3.** *E. faecalis* inactivation by solar photo-Fenton at neutral pH at different solar UVA irradiances, 10 (●), 20 (▲) and 30 W m$^{-2}$ (■). [$H_2O_2$] = 50 mg L$^{-1}$, [$Fe^{2+}$] = 20 mg L$^{-1}$. $T$ = 25 °C. Scatters correspond to average values of log($C/C_0$) for all experiments against experimental time; error bars correspond to standard deviation to average, and straights is the linear fitting of plotted data for each UVA irradiance value.

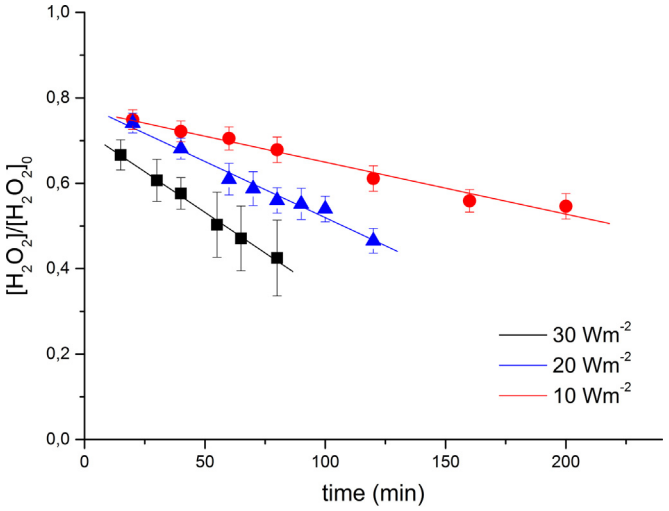


**Fig. 4.** $H_2O_2$ consumption profile during *E. faecalis* inactivation by solar photo-Fenton at neutral pH at different UVA irradiances, 10 (●), 20 (▲) and 30 W m$^{-2}$ (■). [$H_2O_2$] = 50 mg L$^{-1}$, [$Fe^{2+}$] = 20 mg L$^{-1}$. $T$ = 25 °C. Scatters correspond to average values of [$H_2O_2$]/[$H_2O_2$]$_0$ for all experiments against experimental time; error bars correspond to standard deviation to average, and straights is the linear fitting of plotted data for each UVA irradiance value.

$$C = C_0 e^{-k \cdot t} \tag{12}$$

At 10 W m$^{-2}$ of UVA irradiance, the rate constant, $k$, was 0.025 ± 0.002 min$^{-1}$ ($R^2$ = 0.96) and the detection limit was reached after 220 min. At 20 W m$^{-2}$, $k$ was 0.057 ± 0.001 min$^{-1}$ ($R^2$ = 0.98) and 0.089 ± 0.004 min$^{-1}$ ($R^2$ = 0.98) at 30 W m$^{-2}$, reaching the detection limit after 110 and 80 min, respectively. Additionally, the *E. faecalis* inactivation rate constant, $k$, increased in a linear fashion with irradiance (Eq. (13)). These results point out that bacterial inactivation by solar photo-Fenton process at neutral pH was photo-limited, that is, the higher the irradiance, the higher the inactivation rate.

$$k = (30 \pm 1)\,10^{-4} \cdot I_{UVA}; \quad R^2 = 0.99 \tag{13}$$

As for the photo-Fenton reaction at neutral pH most of the added catalyst forms iron hydroxides, removing dissolved iron from the solution. Nonetheless, iron hydroxides in suspension are still efficient for the photo-Fenton reaction as denoted by the hydrogen peroxide consumption in the iron hydroxides redox cycle (Eqs. (9) and (10)) giving rise to hydroxyl radicals as the main ROS. In Fig. 4 the normalised $H_2O_2$ concentration is plotted *versus* treatment time for the three irradiances used in this study, pooling all the data obtained in 18 experimental runs. Regardless of the irradiance value, a drop in hydrogen peroxide concentration was observed in the early stages of the reaction (~25% reduction). This was due to the rapid oxidation of the initially added ferrous iron into ferric iron with the subsequent stoichiometric consumption of hydrogen peroxide (Eq. (1)). Once ferric iron was formed, it generated stable iron hydroxides and the photocatalytic redox cycle started [6,14] and a progressive consumption of the oxidizing reagent was measured. During this second stage of hydrogen peroxide reaction, zero-order kinetics was observed and experimental data fitted to:

$$[H_2O_2] = [H_2O_2]_0 - k_{H_2O_2} \cdot t \tag{14}$$

The hydrogen peroxide rate constant, $k_{H_2O_2}$, at 10, 20 and 30 W m$^{-2}$ of UVA irradiance was (2.5 ± 0.2)·10$^{-3}$ mM min$^{-1}$ ($R^2$ = 0.98), (5.5 ± 0.3)·10$^{-3}$ mM min$^{-1}$ ($R^2$ = 0.98) and (7.9 ± 0.3)·

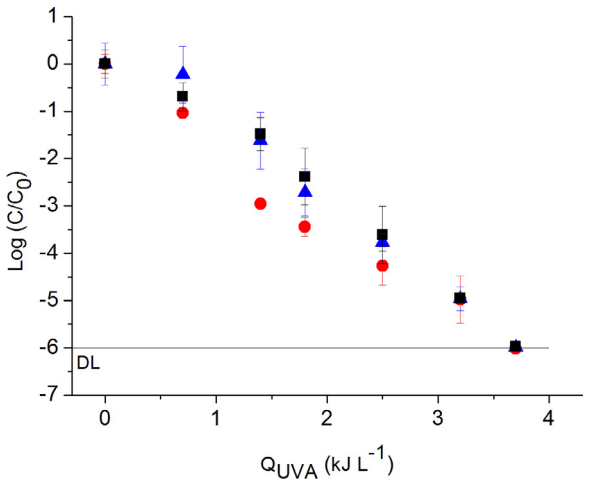


**Fig. 5.** *E. faecalis* inactivation by solar photo-Fenton at neutral pH *versus* accumulated energy dose reached at different UVA irradiations: (a) 10 (●), (b) 20 (▲) and (c) 30 W m$^{-2}$ (■). [$H_2O_2$] = 50 mg L$^{-1}$, [$Fe^{2+}$] = 20 mg L$^{-1}$. $T$ = 25 °C.

$10^{-3}$ mM min$^{-1}$ ($R^2$ = 0.99), respectively. At a given irradiance, the rate of hydrogen peroxide consumption was constant and not dependent on its concentration, but on the photon flux reaching the reactor. An increase in irradiation led to a higher oxidizing agent consumption rate and consequently, a higher hydroxyl radical generation rate (Fig. 4). Furthermore, a linear relationship was observed between $k_{H_2O_2}$ and irradiance expressed by Eq. (15). This shows that the photo-Fenton cycle at neutral pH was photo-limited. Therefore, a clear correlation between *E. faecalis* inactivation and hydrogen peroxide consumption was established, both processes being rate limited by irradiance.

$$k_{H_2O_2} = (2.7 \pm 0.2)\,10^{-4} \cdot I_{UVA} + (1.0 \pm 4.0)\,10^{-4}; \quad R^2 = 0.99 \quad (15)$$

Mechanisms that cause bacterial inactivation during photo-Fenton treatment at neutral pH have been discussed previously [4,10] and can be summarized as follows: (i) the generation of external hydroxyl radicals (Eqs. (1) and (2)); (ii) the diffusion of $Fe^{2+}$ inside the cells along with metabolic hydrogen peroxide leads to hydroxyl radical production *via* internal Fenton reactions.

Considering that *E. faecalis* inactivation rate by solar photo-Fenton process at neutral pH is limited by irradiance; first order kinetics for *E. faecalis* inactivation is expected when the accumulated energy dose is used, as this variable takes into account the integrated irradiance which reaches the reactor surface as well as the solar exposure time (Eq. (11)).

To demonstrate this hypothesis, *E. faecalis* inactivation was plotted *versus* the accumulated energy dose from 0.6 to 3.7 kJ L$^{-1}$ reached at the different fixed values of solar irradiation, that is 10, 20, and 30 W m$^{-2}$. Fig. 5 shows the linear decrease in *E. faecalis* concentration (log scale) with respect to $Q_{UVA}$ regardless of the UVA radiation intensity used to achieve the energy dose (Eq. (16)).

$$\log\left(\frac{C}{C_0}\right) = (-1.65 \pm 0.07) \cdot Q_{UVA}; \quad R^2 = 0.97 \quad (16)$$

In order to achieve the same bacterial damage, when irradiance was lower, a longer exposure time was required. Therefore, *E. faecalis* inactivation could be estimated as a function of the accumulated energy dose in the range of solar irradiance used in this study. According to our results, the accumulated dose is an adequate parameter to evaluate wastewater disinfection under photo-limitation conditions.

For the case of solar heterogeneous photocatalysis by $TiO_2$, Sichel et al. [8] suggested that the efficiency of the processes was driven by $Q_{UVA}$, while the inactivation of different microorganisms was not proportional to UVA irradiance as long as enough energy (kJ L$^{-1}$) was received to achieve the desired disinfection level [8]. On the other hand, Rincón and Pulgarín suggested that *E. coli* photo-inactivation by $TiO_2$ is mainly dependent on UVA irradiance (intensity, W m$^{-2}$), while the solar UV dose is not a pertinent parameter for standardizing solar disinfection [15]. This may be due to the very different experimental conditions used in these studies, such as the type of microorganism and the source of photons and spectral distribution. Ndounla et al. [9] also evaluated the role of irradiance (intensity) and accumulated energy on photo-Fenton process efficiency [9]. They evaluated the effect of the treatment during different periods during the day in natural drinking water, based on the monitoring of the effective disinfection time. They reported a significant effect of the solar irradiance but not the dose during the process. The photo-catalytic inactivation was carried out with very low amounts of iron (a natural concentration found in well water). In this case, using clear water and low iron concentration, the process could be photo-saturated and there was excess of photons to activate the reduction of ferric iron to ferrous iron as reported for micropollutant removal by solar photo-Fenton [14].

According to our results, bacterial inactivation by photo-Fenton is driven and limited by the amount of hydroxyl radical generated, therefore the inactivation rate is limited by the total amount of photons ($Q_{UVA}$) received in the system regardless of the irradiance level. Additionally, after bacterial solar exposure there were no cases of post-treatment recovery, showing that bacterial damage is not due to reversible mechanisms which can be generated by genetic responses to UVA oxidative stress, but irreversible ones, like those caused by hydroxyl radicals [16,17]. In line with this, our findings have clear implications for kinetic characterization and reactor design for disinfection processes.

## 4. Conclusions

Increasing the irradiance on the reactor surface improved the *E. faecalis* inactivation rate by solar photo-Fenton at neutral pH and 20 mg L$^{-1}$ initial iron concentration. The first order rate constants followed a linear correlation with irradiation indicating that bacterial inactivation was photo-limited in the 10–30 W m$^{-2}$ UVA range. This photo-limitation phenomenon was also observed for the hydrogen peroxide consumption rate: a linear relationship was observed between $k_{H_2O_2}$ and irradiance. Therefore, an increase in the radiation intensity resulted in a higher oxidizing agent consumption rate and consequently, in higher hydroxyl radical production, giving an increase in the rate of bacterial inactivation.

As for the accumulated energy per unit volume (kJ L$^{-1}$), this parameter combines irradiance and solar exposure time and consequently, bacterial inactivation follows a first order kinetic with $Q_{UVA}$ regardless of the irradiance. To achieve a given bacterial inactivation degree, the lower the irradiance is, the longer the required exposure time. Therefore, a photo-Fenton treatment plant for wastewater disinfection could be operated on a $Q_{UVA}$ dose basis.

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